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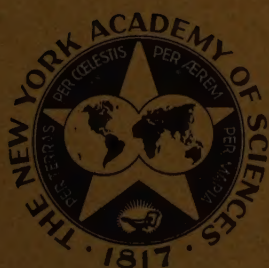
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RECENT APPLICATIONS OF ELECTRON DIFFRACTION

By

J. J. TRILLAT



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RECENT APPLICATIONS OF ELECTRON DIFFRACTION

By

J. J. Trillat

*X-Ray Laboratory, National Center for Scientific Research, Bellevue, France,
and the University of Paris at the Sorbonne, Paris, France*

In this article I shall describe some investigations being carried out in the X-ray Laboratory of the National Center for Scientific Research, Paris, France, related to the development of new methods in electron diffraction. These studies have already furnished new methods for research on the structure of matter, and hence have made a contribution to the progress of science.

The general object of these investigations has been a kinetic study of physical and chemical transformations, diffusion, and reaction phenomena in the solid state. A precise knowledge of these kinetics is of primary importance in a large number of theoretical and technical problems. Such problems, when investigated by classical means, require, in general, much time and give only indirect information. On the other hand, the unique methods of electron diffraction, with certain modifications, permit a successful solution of these problems.

There are several approaches, including the intermittent or semi-continuous method of observing phenomena, and the continuously recorded or continuous method. This paper describes these two methods, including the method of ionic bombardment, which is a semicontinuous method.

Two instruments are used in our laboratories. One of them, the older, has a hot cathode. The other is an electron diffractor with a cold cathode, built in Zurich, Switzerland, by Trub Tauber, which we have modified in many ways (FIGURE 1). FIGURE 2 shows the design of the heating part of the Tauber instrument, which allows reflection and transmission experiments to be made up to a temperature of about 1000° C.

The Semicontinuous Method and its Application

This is a well-known method. For a long time many workers have used electron diffraction to follow the various stages of a chemical or physical transformation.

If the structure of a substance is being modified by a physical or chemical agent, the electron diffraction patterns produced are easily registered intermittently. A comparison of the results will give the course of the reaction. In this way, the substance can be examined outside of the instrument or periodically introduced into the instrument for examination. The substance may be manipulated inside the instrument, however, and results obtained in this way are particularly interesting. Much

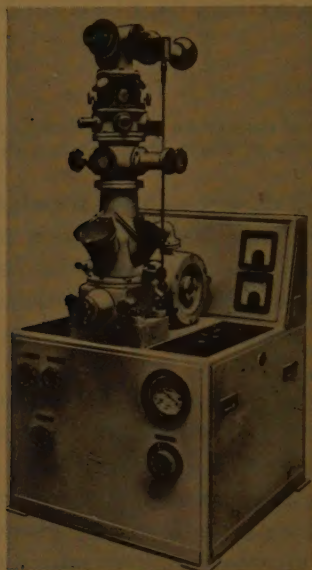


FIGURE 1. Electron diffraction unit of Trub and Tauber, Zurich, Switzerland.

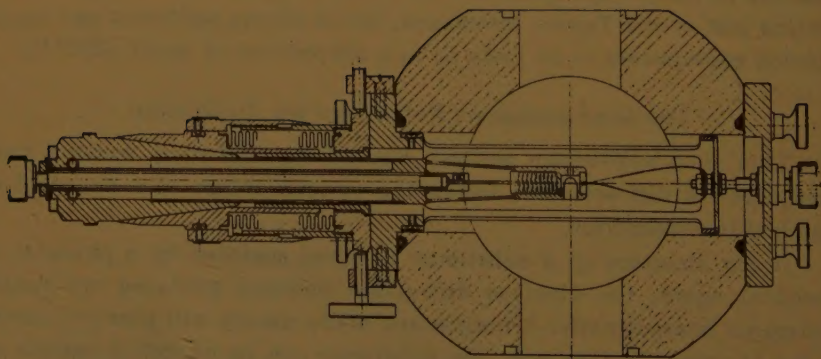


FIGURE 2. Drawing of heating table. The sample is placed in the middle of the oven and heated electrically. Temperature is measured by thermocouple.

work has been done by means of this method, mostly on the oxidation of metals, particularly by E. A. Gulbransen, R. W. Hickmann, S. Miyake, O. Abe, S. Ogawa, and R. C. French.

The oxidation of some metals can be observed by thermal evaporation inside the electron diffraction instrument. As all present instruments are of the "kinetic" vacuum type, the remaining gases, under a pressure, usually, of 10^{-3} to 10^{-4} mm., are oxygen, nitrogen, and traces of moisture. The oxidation is more readily observed when metals having great affinity for oxygen are vaporized in a partial vacuum. This is particularly true of "getter" metals but not at all for noble metals. The first layers of evaporated metal mostly give the diagram of the oxide. The diagram of the metal itself appears only at pressures less than 10^{-5} mm. There are true threshold temperatures characteristic of the metal, above which the metallic layers are oxidized very quickly. Further applications will be described under the continuous method.

Adsorption of fatty substances on metals. I previously showed that organic molecules with long chains, such as fatty acids, paraffins, alcohols, and waxes are capable of being fixed on metallic surfaces, and that they are oriented normally or slantwise to the surface. These layers, which can be only monomolecular or bimolecular, are readily detected by electron diffraction, and they are detected as easily by transmission as by reflection (FIGURE 3). They give characteristic patterns, the electron being diffracted by carbon atoms regularly disposed along the hydrocarbon chains. Such studies give the precise condition of formation of the layers and have been applied to lubrication phenomena.

It seems that the orientation of these molecules would be made easier by a chemical reaction if this were possible. For instance, when even an extremely small quantity of a fatty acid is spread on the surface of metals that are readily attacked, such as iron, copper, and lead, a very thin intermediate layer is formed by the fatty acid plus the metal compound: in other words, a layer of soap. Electron diffraction X rays show the presence of this soapy layer when it exists. Contrary to what would be thought, this soapy layer plays an important part in lubrication by lowering the friction factor; one has therefore to facilitate its creation by adding to lubricating oils compounds such as fatty acids or molecules ("dopes") able to attack the metal, however slightly.

Electron diffraction allows study of the details of the formation of these layers, which are more easily made in the presence of air or moisture than *in vacuo*; one can also study their behavior as a function of temperature, which is essential for lubrication.

Recent investigations carried out in England by F. P. Bowden and G. I. Finch permitted study, with precision, of the structure and the orien-

tation of films formed by fatty acids and soaps adsorbed on metallic surfaces.

In using the method of reflection, the temperature effect on the orientation of adsorbed molecules was examined. The results prove that, at room temperature, the first layer is generally oriented in such a way that hydrocarbon chains are arranged normally in support. When the temperature is increased, diagrams become more and more diffuse and, after a characteristic temperature, only the diagram of the support is observed. This transition is due to a disorientation effect, since, on cooling, the orientation of hydrocarbon molecules is again observed. At elevated temperatures, the superficial film can even be completely vaporized.

If fatty acids are spread on an unreactive metal such as platinum or gold, the disorientation temperature is the melting point of the fatty acid. On reactive metals such as zinc, cadmium, and iron, the disorientation occurs at a higher temperature that coincides with the melting point or softening point of the corresponding metallic soap, indicating the formation of this soap by a chemical reaction. The friction factors are directly connected with these changes in the structure and orientation of the intermediate layer, and they exhibit sudden discontinuities at the transition point.

The alteration of metallic surfaces by the various compounds now added to lubricating oils (sulfone derivative, tricresyl, or triphenyl phosphate) can also be followed as a function of time or of temperature. The composition of the attacking layer, which has also a protective role, can thus be determined, showing how the semicontinuous method can be applied with profit to important problems such as lubrication.

Investigation of the transformation produced by the action of electrons. It is well known that transformations produced by electron bombardment are due to several causes: to heating, to ionization, and to photochemical effects. This last effect is the most interesting and, for this reason, the action of electrons on silver bromide was studied. A thin film of AgBr was prepared by evaporating (FIGURE 4), *in vacuo*, a small quantity of the compound and by condensing the vapor on an amorphous or crystalline support (NaCl). In the first case, the bromine crystallizes in a microcrystalline form and gives a Debye-Scherrer diagram (FIGURE 6). As a result of the interaction between the NaCl and AgBr, an extremely thin monocrystal is formed in the second coil (FIGURE 5).

The action of the electron beam, hitting the substance always at the same point, results in the more or less rapid liberation of metallic silver, the increase of which can be followed directly on the fluorescent screen or can be registered photographically (FIGURE 6). Thus electrons

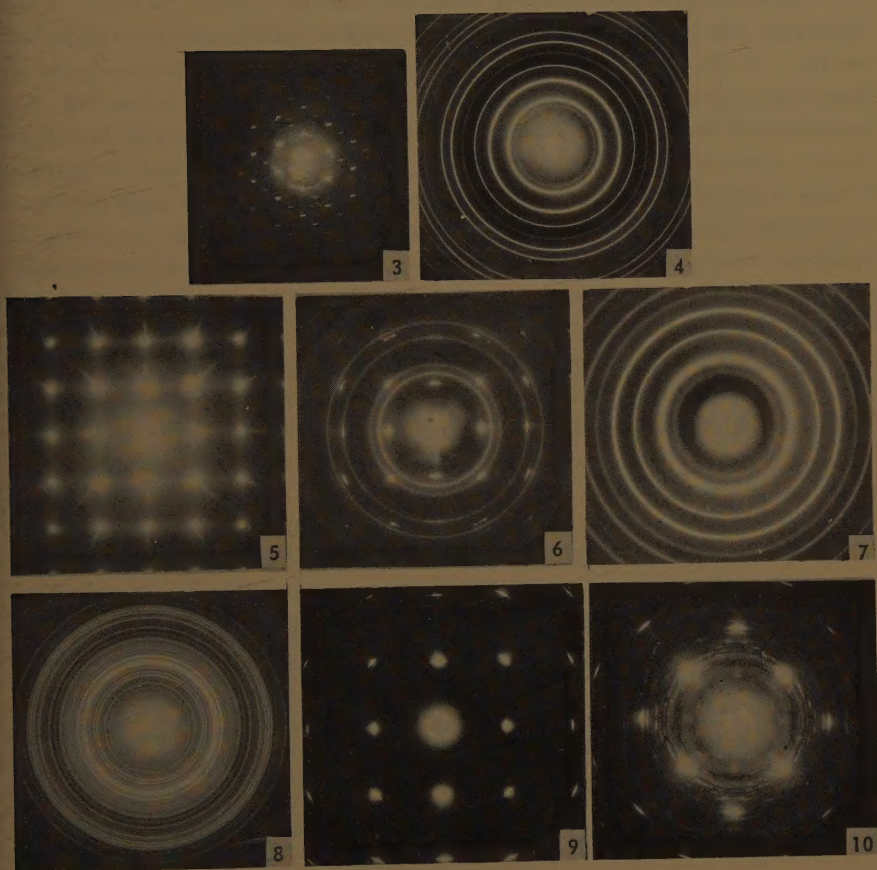


FIGURE 3. Diffraction pattern of a uniaxial layer of paraffin.

FIGURE 4. Polycrystalline AgBr.

FIGURE 5. Uniaxial AgBr (OO^2 -plane perpendicular to the electron beam).

FIGURE 6. Formation of unoriented silver (ring diagram) by action of electrons on a uniaxial layer of AgBr (isolated spots).

FIGURE 7. α -Fe; polycrystalline (body centered).

FIGURE 8. Cementite Fe_3C (orthorhombic).

FIGURE 9. α -Fe; uniaxial.

FIGURE 10. Formation of oriented cementite Fe_3C (interrupted rings) from uniaxial α -Fe (isolated spots).

act as a reducing agent and, at the same time, are diffracted by the same substances that they produce.

The photographic action of electrons can be studied in detail. One finds that the liberation of silver is a function of the electron beam intensity, of the thickness of the substance and, mainly, of the more or less high perfection of the crystalline network. Generally speaking, the less perfect the crystalline structure is, the more rapid is the decomposition; moreover, the liberated silver does not show, except in certain cases, a specific orientation related to the network of the AgBr crystal. The same process can be followed by using reflection on a large crystal of silver halide. By this process one can even follow the effect of light radiation on the crystal and show that the silver liberated on the surface has the same structure in depth (D. W. Pashley, Berry).

By making extremely thin layers of photographic emulsions, one can follow the same phenomena and confirm the previous results. One can even show the optimum structure of grains in emulsion. These investigations can be complemented by simultaneous studies using the electron microscope.

A study of the cementation of iron. It is known that the cementation of iron is a process resulting in a superficial hardening of the metal through the formation of cementite Fe_3C . Cementation occurs in various industrial processes, such as the action on the metal of carbon monoxide, pure or mixed with hydrogen, at a high temperature.

My collaborator, S. Oketani, and I have investigated the different stages of formation and decomposition of cementite, working with iron films produced by thermal evaporation *in vacuo*. On these films, 100 to 200 Å thick, were carried out all the procedures of industrial cementation, with either pure carbon monoxide or a mixture of carbon monoxide and hydrogen.

It was thus possible to follow all steps of the process and to determine the temperatures of the appearance and disappearance of the compound Fe_3C . FIGURES 7 and 8 show first the diagram of pure iron (nonoriented polycrystalline), then, above 450°C ., the diagram of orthorhombic cementite, the latter being decomposed in iron and graphite at temperatures above 650°C . The presence of hydrogen in the gas plays an important role that cannot be dwelt on here. Hydrogen, particularly, facilitates the formation, at lower temperatures, of unstable carbides (Fe_3C , Haff carbide) that exist only in a limited range of temperatures (350°C . to 400°C .). These percarbides, of whose structure little was known, play an important part in the catalysis, by iron, of mixtures of $\text{Co} + \text{H}_2$, the basis of great organic syntheses.

In preparing extremely thin monocrystals of iron, we could follow

the appearance and the development of cementite at the expense of the crystal, and thus deduce the relationship of orientation between iron and the carbide Fe_3C , characterized by arcs which, as the reaction proceeds, become disoriented and finally give the ring diagrams of the cementite shown in FIGURES 8, 9, and 10.

We chose this example of iron cementation as being particularly typical, but of course, a similar technique can be used for the study of other surface reactions, such as nitration.

Structure and properties of fresh surfaces. The surfaces of the majority of substances are naturally imperfect because of various impurities that are extremely difficult to avoid, such as oxides or hydrated films, contamination layers due to fatty substances, and adsorbed gases. The presence of these impurities can greatly modify the behavior of the substance, especially concerning its chemical reactivity and its adsorption or catalyst properties. Therefore, it seems, a priori, of great interest to try to prepare surfaces purified of all contaminants, to study their structure and various properties.

This investigation was carried out in my laboratory by R. Courtel, who succeeded in obtaining, by vacuum grinding inside the electron diffraction instrument itself, freshly contaminated metallic surfaces and in following simultaneously the remarkable adsorption phenomena occurring on such surfaces. Besides determining the crystal structure obtained under these conditions, R. Courtel also studied allotropic transformations of cobalt and showed the existence of a limiting grinding speed beyond which the transformation occurs. The introduction of traces of oxygen allowed him to follow the progressive oxidation of cerium and to prove the existence of the oxide Ce_2O_3 , which X rays could not show. Finally, the introduction of a small quantity of hydrocarbon was manifested by the immediate fixation of these molecules on the fresh metallic surfaces, with an orientation provoking an actual "crystallization" of the hydrocarbon. The application of this finding to lubrication is obvious.

All these researches were made possible by the study and adjustment of a delicate device permitting the grinding of a metallic surface *in vacuo* with a grinding stone spinning at 45,000 rpm. and working with successive cuts, the thickness of which was controlled by means of cathodic oscillograph.

Atom diffusion and transformation of alloys. Another way of getting a fresh surface is to evaporate thermally, *in vacuo*, the atoms forming a mixture or an alloy, and to condense these atoms on an appropriate support. According to the nature and temperature of this support, it is possible to follow the evolution of the structure of the layer and, if

different atoms are vaporized, to study their diffusion as a function of time and temperature.

Much work has been published by investigators using this technique; among others, by L. H. Germer, H. Raether, A. Boettcher, S. Ogawa, S. Goldzstaub, P. Michel, J. J. Trillat, and N. Takahashi.

Several different techniques may be used but, in essence, the 2 metals are evaporated *in vacuo*, either from a simple source or from 2 distinct sources. The vapors are condensed on supports of rock salt previously cleaned and brought to a given temperature. The metallic film is then studied by electron diffraction after discovering its support in water.

By evaporating aluminum and copper simultaneously from 2 sources and by condensing them on a cold support (20°C.), one gets only a mixture of the 2 metals in various proportions, according to the position of the support relative to the 2 sources. The mobility of the Al and Cu atoms is therefore too small at this temperature to allow the formation of a compound or of a solid solution. If, on the other hand, the condensation takes place on a support at 300°C. , one gets, according to the position of this support, different patterns extremely rich in lines. It is thus possible to identify with precision many compounds, such as CuAl_2 , which are directly formed under these conditions.

By using a simple source and evaporating, on a cold support (20°C.), known mixtures of the 2 pure metals, one gets only diffuse patterns (FIGURE 11), indicating the formation of extremely small heterogeneous crystals, strongly distorted and not in equilibrium. This phenomenon resembles the disturbed homogeneity described by P. Chevenard and A. Portevin. On aging, these structures become refined and produce definite phases, among which one observes the oriented *O* phase (CuAl_2). On a hot support (300°C.) one gets, according to the composition of the mixture, extremely clear patterns (FIGURES 12 and 13), where one finds the main phases of the equilibrium diagram (CuAl_2 , CuAl , Cu_3Al_4 , etc.) with indications of superstructures.

By evaporating the alloy itself, for example CuAl_2 , one gets, on a cold support, the same results as with the mixture of the same composition (FIGURE 11). The initial network CuAl_2 is thus completely dissociated during the evaporation. On aging (1 month at 18°C. or 30 minutes at 300°C.), the compound CuAl_2 appears with indication of the *O'* phase. By contrast, on a hot support beyond 200°C. , the tetragonal structure of CuAl_2 is immediately reformed.

We were thus able to explore in detail all the domains of the equilibrium diagram (copper-aluminum). The results show the rich possibilities of this method of studying phases of the alloy, and also of their formation and transformation kinetics.

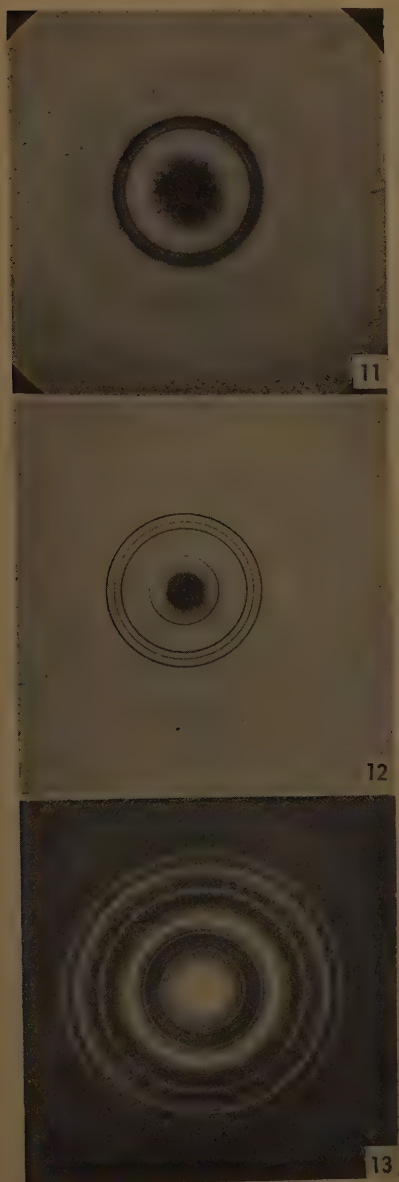


FIGURE 11. Simultaneous evaporation of 50 per cent Cu and 50 per cent Al on a cold support.

FIGURE 12. Al_2Cu obtained by evaporation of 50 per cent Cu and 50 per cent Al on a hot support at 300°C .

FIGURE 13. Al_4Cu_9 , obtained by evaporation of 80 per cent Cu and 20 per cent Al on a hot support.

*The Continuous Method of Recording Physical or
Chemical Transformations*

We shall now discuss more recent developments of electron diffraction by which it is possible to observe continuously the variations of structure of substances provoked by physical or chemical action.

In the "semicontinuous method," the electron diffraction patterns are separately obtained. The various stages of a reaction or of a transformation are recorded, but not continuously. The continuous recording of these stages is a question of great interest in many fields, theoretical as well as practical. As early as 1935, I used for this purpose a photographic film moved, during exposure, in a plane perpendicular to the electron beam. The results obtained were greatly improved, as shown by A. Boettcher, by concealing the film with a metallic plate having a thin slot located at the impact point of the nondiffracted electron beam. The film was now moved by an electric motor containing a reduction gear, so that the optimum speed (several cm./mm.) could be obtained. Boettcher and R. Thun recently applied such a device to the study of the evolution of this metallic layer.

Let us see what happens when a pattern composed of Debye-Scherrer rings is studied by means of such a device. It is obvious that, in such circumstances, the photographic emulsion receives only the electrons passing through the slit and located along small arcs, the lengths of which are equal to the opening of the slit. Due to the displacement of the film, these arcs are registered as parallel lines, the thinness of which is a fraction of the width of the slit, and their intensities are in the same ratio as in the complete pattern. Therefore it is easy, after development, to interpret the exposed film in the same way as the Debye-Scherrer ring patterns.

FIGURE 14 illustrates the described device, which can also be used in applying the reflector technique. This method is of great interest when, for example, one has to follow the variation of alloy structures as a function of temperature. For that purpose, the alloy film is put on the heating support (capable of being heated up to 1000° C.) and is examined by transmission.

The temperature recording is easily done by illuminating the photographic emulsion, through the slit, every 50 degrees, for instance. These temperature marks can be complemented by time marks. The Trub Tauber Company makes a camera especially modified for this method.

We thus have a complete record of the evolution of many alloy phases prepared by evaporation *in vacuo* of Cu and Al that we had previously studied by the semicontinuous method. FIGURE 15 shows an example of continuous recording obtained from a mixture of 50 per cent

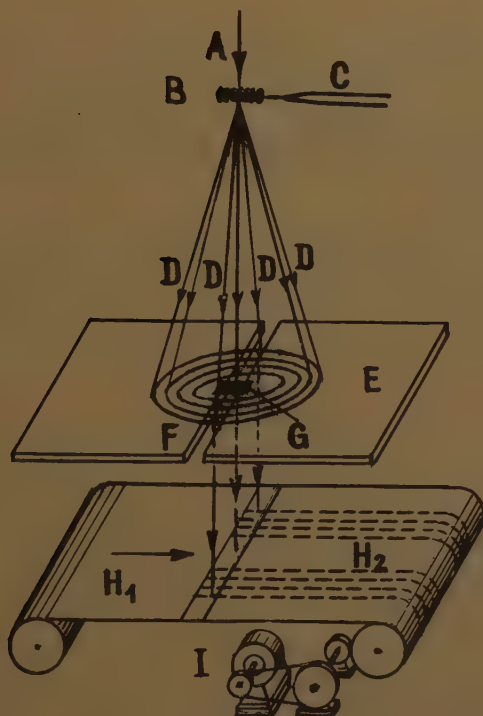


FIGURE 14. Sketch of the continuous registration method: (A) primary electron beam; (B) hot plate with sample; (C) thermocouple; (D) diffracted electron beams; (E) metal plate; (F) adjustable slit; (G) dead stop for primary beam; (H₁) original photographic film; (H₂) exposed photographic film; and (I) motor for film motion.

aluminum and 50 per cent copper in which one clearly sees the change from a more homogeneous structure with a c.f.c. network (characterized by diffuse lines) to a definite compound CuAl_2 (O phase of the equilibrium diagram), characterized by the thin rays of a quadratic network. It is interesting to notice the disturbed homogeneity that occurs shortly before the crystallization of the CuAl_2 compound. Its detailed study may yield interesting information as to the mechanism of structural hardening (compare with FIGURES 11 and 12).

FIGURE 15 refers to the evolution, as a function of temperature, of a mixture formed by 90 per cent aluminum atoms and 60 per cent copper atoms; one can see the rapid transformation, around 370°C . of the initial phase, of the imperfectly crystallized mixture becoming a definite compound, which is here CuAl (FIGURE 16).

Another application of the method was made by A. Boettcher. Let us

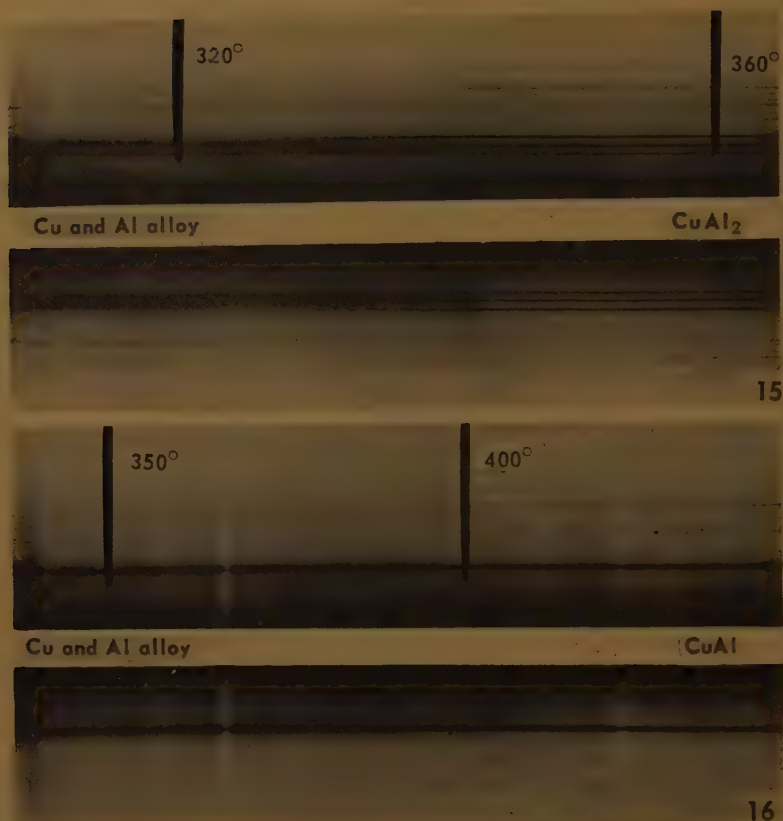


FIGURE 15. Continuous registration of transformation of 50 per cent Cu and 50 per cent Al into Al_2Cu tetragonal (see also FIGURES 11 and 12).

FIGURE 16. Continuous registration of transformation of 60 per cent Cu and 40 per cent Al into cubic AlCu .

assume that one deposits, by evaporation *in vacuo*, 2 layers forming wedges in opposite directions, as indicated schematically in FIGURE 17. When such a setting is heated, the diffusion equilibrium is very rapidly established in the direction perpendicular to its plane, the total thickness being only a few angstroms. The diffusion in the plane of the layer, on the other hand, is very negligible. In exploring this sample with an electron beam perpendicular to the support and in synchronizing it with the displacement of the photographic film, one gets on the film an ensemble of lines related to the various phases corresponding to different atomic concentrations. FIGURE 17 shows the obtained pattern schematically. This process was applied by Boettcher to a study of the diffusion of gold and tin. Before heating the sample, one sees only a mix-

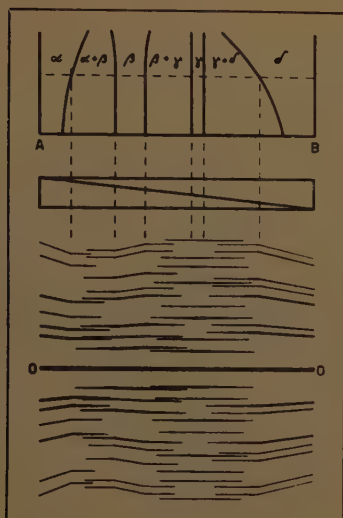


FIGURE 17. Sketch of the Boettcher method. On top is equilibrium diagram of Au + Sn. Below is registration at various points of formation.

ture of the diffraction lines of the two metals. After being diffused by heating, all phases of the Au-Sn system appear. By thus making "cuttings" through a mixture of the 2 constituents, there is the possibility, especially in the domain of low temperatures, of obtaining information concerning the equilibrium diagram and of showing many phases heretofore unknown.

We used this technique in many other cases also, as in studying the transformation of amorphous antimony into crystalline antimony (FIGURE 18). In these experiments, antimony was evaporated on a collodion support at room temperature, then heated in the electron diffraction unit. It is interesting to notice that the initial structure of Sb is amorphous, for the diffraction rings of the crystalline Sb (rhombohedral) further a transformation that is irreversible.

We can now assert that the continuous recording method can be used in many applications, as in studying the diffusion of different atoms, the evolution of alloys with apparent phases, structural hardening and aging, the transformation of crystalline structures at varying temperatures, the passage from an amorphous state to a crystalline state in detail, the decomposition of substances by heat, the study of stability zones, and various stages of the dehydration of a compound. There are also applications in organic chemistry and polymer chemistry; thus we have succeeded in recording continuously the variation of the per cent of crystallinity of polythenes and their passage through the transition point

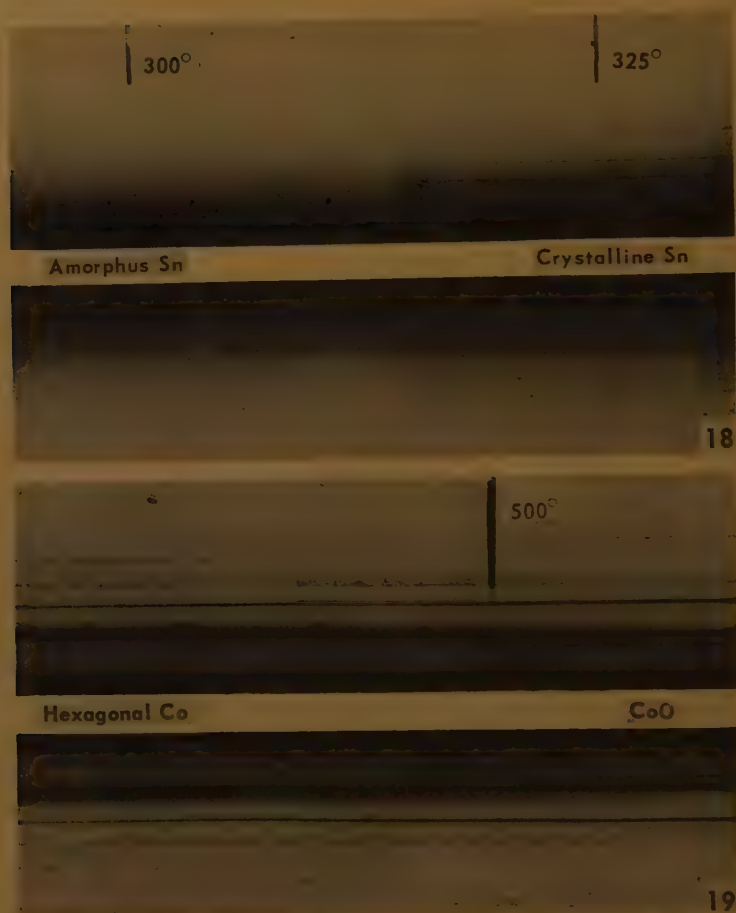


FIGURE 18. Continuous registration of transformation of amorphous Sn into crystalline Sn.

FIGURE 19. Oxidation of hexagonal Co to cubic CoO.

115° C.), where they become completely amorphous. The fact that traces of gases are always present in the instruments used leads to many other applications. Thus the presence of oxygen permits one to follow oxidation reactions as a function of temperature and pressure. We have thus followed the oxidation of cobalt, which is hexagonal at low temperature but is transformed at high temperature into the (cubic) oxide CoO (FIGURE 19). In the same way we followed the oxidation of aluminum into alumina (FIGURE 20). The case of zinc is interesting. Near its melting point, the film of hexagonal Zn is transformed suddenly into ZnO, which is also hexagonal (FIGURE 21).

Finally, we have begun experiments that permit the introduction into the instrument of various gases (e.g. N_2 , Co, Co_2 , H_2 , etc.). Trials with argon showed that one can suppress completely the phenomenon of oxidation, which is almost unavoidable because of the presence of small quantities of air even at a very low pressure (10^{-4} mm. Hg).

We thus hope to follow certain technically important reactions, such as cementation and nitration. In many cases, the sample can be prepared inside the instrument itself by thermal evaporation of the constituents. Hence whole evolutions, beginning with the time when the atoms or molecules are condensed on a support, may be recorded.

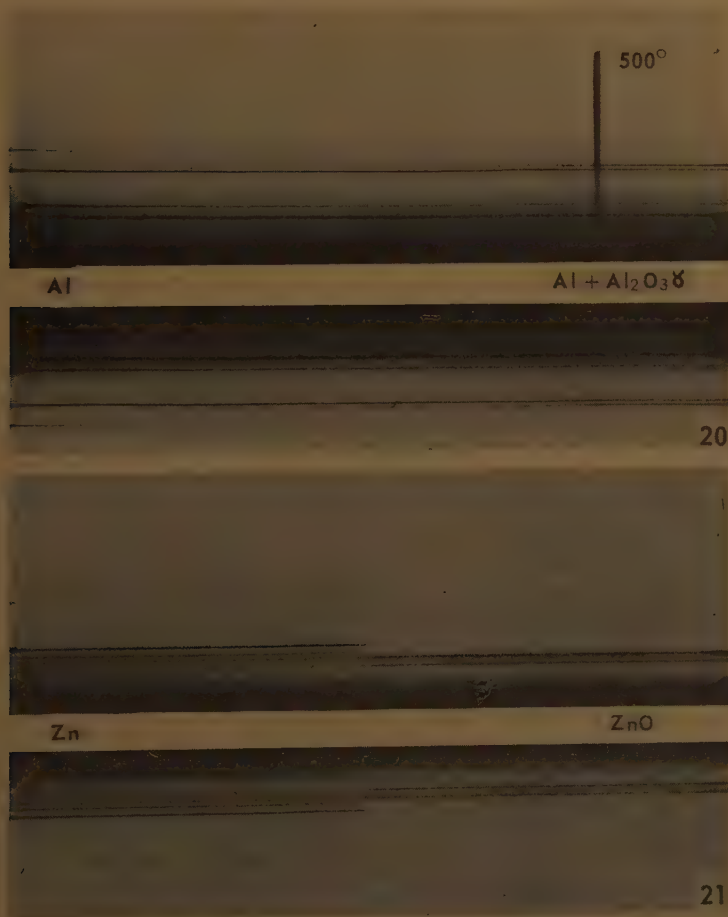


FIGURE 20. Oxidation of Al to α - Al_2O_3 .

FIGURE 21. Oxidation of Zn to ZnO.

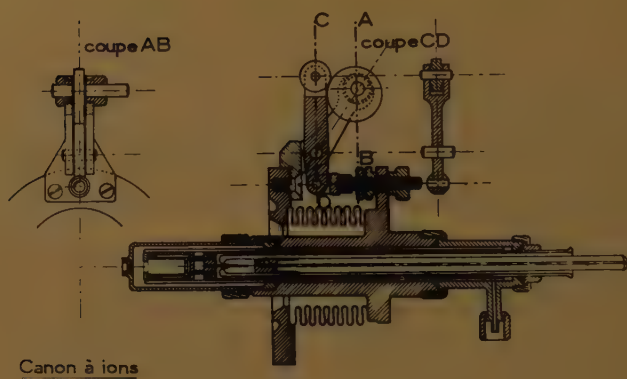


FIGURE 22. Sketch of the "ion gun."

The Method of Ionic Bombardment

Finally, I shall discuss a very recent method that can probably be greatly developed for industrial application. This is a process of attacking surfaces based on bombardment by rapid ions. The first investigator to apply this process to electron diffraction was C. Fert, whose method has been improved in my laboratory.

The ion gun is a tube for electric discharges in a rarefied gas. Its design is inspired by the electron gun of the electron diffraction unit having a cold cathode. Its shape is that of a cylindrical tube attached to the aperture of an electron diffractor or of an electron microscope. The hole pierced in the cathode along the tube axis is so small that the pressure does not exceed 10^{-4} mm. Hg. inside the instrument. A simple orientation device allows aiming at the object. FIGURE 22 shows the scheme of the ionic gun built in the laboratory, one that can be fed by various gases (air, argon, nitrogen, and others). This gun gives an ionic beam of 10 to 20 amp. for a total current of 200 amp. and a voltage of 25 kv.

The ionic bombardment of an observed object by reflection presents the following possibilities in electron microscopy:

- (1) As is already known, it completely eliminates static charges during the examination of insulating materials and avoids contamination. It is enough, for that purpose, to accelerate ions with a voltage of only 1 to 3 kv.
- (2) Ionic bombardment is the scouring and the superficial thinning of the object. This phenomenon, known as cathodic pulverization, has been used for a long time, either to obtain this metallic layers or as an at-

tacking process in metallography (H. Feitknecht, R. D. Heidenreich, R. Castaing).

The ionic bombardment of an object allows the progressive removal of successive layers from the surface of a sample, keeping a very clean surface in the region hit by the beam without any modification of structure as in electrolytic polishing, and all this during observation by electron diffraction or microscopy. It is thus possible to follow continuously the structure of layers of increasing depth.

This method of "scouring" surfaces by ionic bombardment can be used with ions of different natures: oxygen, argon, etc. The nature of the gas has an influence on the speed of pulverization and on the appearance of certain chemical reactions. It is necessary to take account of the thermal effect produced by the bombardment: for instance, the O^+ ions accelerated by a voltage of 25 kv. and concentrated on a copper area of 4 to 5 mm.² produce when equilibrium is reached, an increase of temperature of about 250° C. Finally, the method can be combined with the continuous recording method previously described.

Experiments are presently being carried out in my laboratory to determine the possibility of this new method. I shall cite some of the more characteristic experiments.

(1) A fresh cleavage surface of a NaCl crystal (200) is mechanically roughened by an abrasive. If one bombards this surface with an ionic beam of 25 kv. (air), one can follow the progressive change from the perturbed layer (Debye-Scherrer) rings to the internal unicrystalline layers (FIGURE 23). The ion beam is used at the same time to eliminate static changes on the NaCl. The experiment can be seen very well on a fluorescent screen.

(2) A brass surface was oxidized in air. Examined at a low angle of incidence, without ionic bombardment, it gives the pattern of polycrystalline ZnO. Under ionic bombardment, one observes the progressive change from ZnO to Cu_2O , then to Cu, or, more exactly, to the solid solution Cu-Zn.

(3) A metallic surface, carefully polished, gives an amorphous pattern due to the superficial Beilby layer. By ionic bombardment, the structure of the metal existing under this layer successively appears. It is seen, by this example, that the method is of great interest in the study of polishing and superficial treatment of metals.

(4) Transmission technique can be used with a thin film forming a 45° angle with the electron beam and the ion beam. Under these conditions, the heating is less. Also, one gets complete patterns.

A film of pure polycrystalline nickel is thus transformed instantly into a film of NiO if it is bombarded by oxygen ions. In an argon atmos-

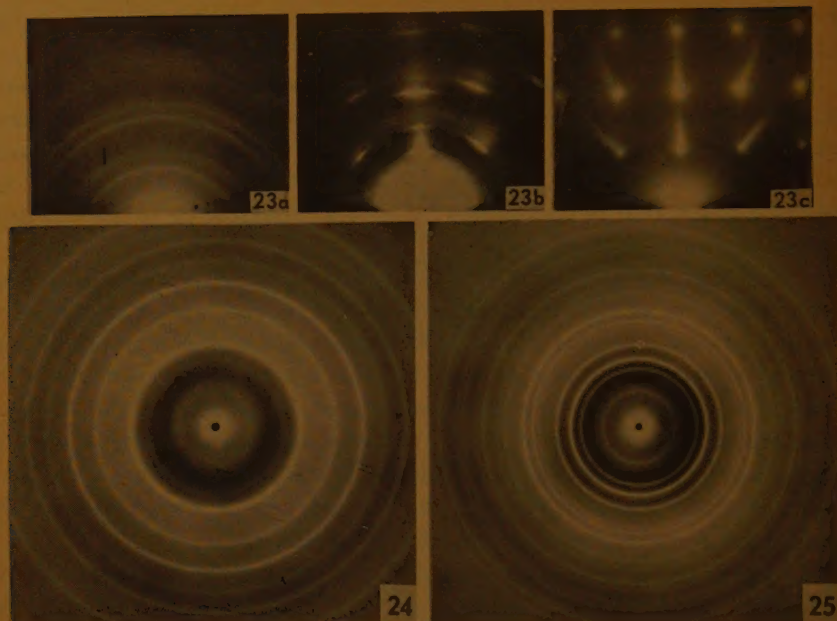


FIGURE 23. (a) polycrystalline NaCl obtained by destruction of a single crystal; (b) intermediate fibrillar structure; and (c) original single crystal of NaCl.

FIGURE 24. α -Fe before bombardment with O^+ ions.

FIGURE 25. Fe_3O_4 obtained by ionic bombardment (O^+ ions) of α -Fe.

here, on the other hand, oxidation does not occur.

Similarly, a film of polycrystalline iron, bombarded by oxygen ions, gives, after 2 seconds, the oxide Fe_3O_4 (FIGURES 24 and 25).

This method is presently used by Fert for electron microscopy and by ourselves for electron diffraction.

The investigation described in this paper shows that it is clear that electron diffraction can be adapted without too much difficulty to the study of the kinetics of a large number of chemical reactions or of physical and physiochemical transformations. The information obtained thus far is encouraging, and it seems that the method of continuous recording of ionic bombardment is an important contribution to the study of various problems such as diffusion, allotropic transformations, the structure of alloys, and surface states in general.

This method that has been initiated merits being followed up, and we hope that this article, while unavoidably incomplete, will induce more workers to explore it.

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